NEW DATA ON NONSTOICHIOMETRIC ALUMINA - ISOTHERMAL VARIATION OF THE ELECTRICAL CONDUCTIVITY AS A FUNCTION OF OXYGEN PRESSURE

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ABSTRACT

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The electrical conductivity of nonstoichiometric alumina is investigated at constant temperature as a function of oxygen pressure. Experiments at $380°C$ reveal in alumina the presence of atomic Al. The log σ is found to be a function of the log P_{O_2} in alumina when Al^+, Al^{+2} ions, and metallic Al are present in the interstices.

The departure from the valence rule of hydrated amorphous alumina (ref. 1) /87*
or of the δ compressed (ref. 2) and vacuum-annealed δ-phase was evaluated direct-
ly by the loss of oxygen or manganometrically. This reducing character was at-
tributed to the existence of metallic Al resulting from the thermal disassocia-
tion process under vacuum and involving the emission of H_2 during the dissolu-
tion of HCl.

From previous studies (ref. 3) where we did not notice significant emis-
sion of gas while dissolving the black and gray samples of nonstoichiometric
alumina, we discussed the probability of the existence of metallic aluminum in
the samples and considered the alternative presence of lower-valence oxides.
At the same time, we demonstrated that the problem has not been sufficiently
studied in the literature and in the present note we are returning with new
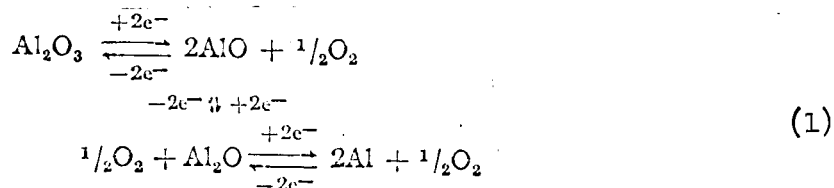experimental evidence.

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*Numbers in the margin indicate pagination in the original foreign text.

We face the problem of establishing the chemical composition and structure of the product with the oxygen deficit obtained by vacuum-annealing of alumina. In principle, there are several possibilities, such as:

1. The existence of dispersed atoms or aggregate granules of metallic aluminum in the base alumina.

2. Existence of lower oxides associated with the alumina.

3. Coexistence of aluminum atoms with lower oxides and alumina.

The presence of alumina is unquestionable and need not be discussed, because, as we showed (ref. 3), the transformation process took place only in the surface layer. It is an established fact, however, that the alumina itself from the deficient product, annealed at 900°C, well crystallized, suffers a radical structural transformation during the vacuum annealing, acquiring an amorphous structural condition in x-ray diffraction even without appreciable nonstoichiometry.

It remains to be discussed if the gray and the black as well as the reducing characteristic of nonstoichiometric alumina is attributable to aluminum or to some lower-valence oxides of alumina. Third hypothesis would be the posi- /88 bility of a discussion based on thermodynamic data on the equilibrium series:

$$Al_2O_3 \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} 2AlO + 1/2 O_2$$
$$-2e^- \updownarrow +2e^-$$
$$1/2 O_2 + Al_2O \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} 2Al + 1/2 O_2 \tag{1}$$

The opinion of H. Juillet and his associates is also accepted by R. Faivre (ref. 4), who considers that the nonstoichiometric product is probably analogous to the black magnesium hydrate and nonstoichiometric oxides of An, Cd, Ag studied by him and his associates (ref. 5, 6 and 7); the conclusions were

generalized and substantiated from x-ray difraction studies on the crystalline

products and nonstoichiometrics, noticing that an increase takes place in the

lattice constants of the nonstoichiometric products (e.g., normal brucite,

a = 3.135 Å, black hydrate, a = 3.142 ± 0.002Å. Confirmation resulted from

thermodifferential analysis, showing as a result that the metallic Mg bucita

forms an insertion lattice, which explains the increase in lattice parameters.

On the other hand, authors demonstrate that in conditions more or less

similar to ours in obtaining nonstoichiometric alumina, one obtains lower oxides

of alumina of dark gray color. Thus M. Piochon (ref. 9) finds that by oxida-

tion of alumina in a hydroxy flame with a slight oxygen deficit a gray-black

product is obtained by incandescence in which the ratio $O: AL \approx 0.6$ and which

by dissolution in HCl emits H_2. The conclusion he arrives is that it has to do

with the mixture of Al, Al_2O and Al_2O_3. The general formula is $Al_6O_7 =$

$= Al_2O3Al_2O_3$.

A. Duboin (ref. 10), as well as Kohn and Abrest (ref. 11) find that the

quantity of oxygen in the gray granulated product visible in Al, whichdissolves

in HCl with effervescence, must be a suboxide of the type AlO.

The bibliography indicating the existence of these suboxides is quite exten-

sive (ref. 12), we mention only that data for the existence of these oxides

was reduced by spectral means (refs. 13 and 14).

Recently E. Gastingen (ref. 15) prepared Al_2O in pure form by annealing at

1300°C of a mixture of 2.3 g AL with Al_2O_3 in an atmosphere of CO and CO_2 (50%)

at a pressure (steam) of 0.02 mm Hg.

M. Mettre (ref. 16) shows that by distillation in vacuum (10^{-5} mm Hg) at

1600°C of impurities in iron powder, Al and Si disappear in vaporization and

settle on the cold parts of the vessel in the form of Al_2O and SiO.

K. Yamaguki and H. Yanagida (ref. 17), by reducing Al_2O_3 with graphite at 1600°C, obtain a black composition which has a reducing character; its formula is Al_4O_4, with spinel structure $-AlO \cdot Al_2O_3$.

By spectral means, Ogurtsova and Posmoshenski (ref. 18) describe the absorption bands of the AlO molecule as visible, then V. H. Goodlet and K. K. Innes (ref. 19) induced electric discharges on $Al-Al_2O_3$ pellets, which having been inserted in a hollow capsule, exhibited evidence on the emission spectrum of the AlO molecule.

Finally, M. G. Inghram and co-workers (ref. 20), by mass spectometry of /89 the vapors and resultant gases from the construction materials used in reactor technology at 2000°K and pressure of 10^{-7} atm, found equilibrium between $Al_2O_3^+$, $Al_2O_2^+$, Al_2O^+, AlO^+, O^+, Al^+, resulting from ionization of the respective molecules and atoms. As far as the oxides AlO or Al_2O_2 are concerned, Inghram proposes the structural formula

$$0 = Al - Al = 0 \text{ și } Al \overset{\displaystyle 0}{\underset{\displaystyle 0}{\diamondsuit}} Al \qquad (2)$$
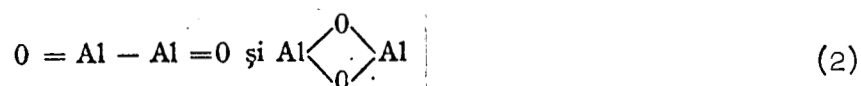
Juillet, and Teichner (ref. 2) in one of their latest publications, seem to favor disordering of the lattice of the nonstoichiometric composition as due to the migration of aluminum atoms and ions in the loose lattice with a tendency toward spiral structure formation, being more deficient in oxygen ions, which would presume the existence of bivalent or monovalent ions.

In order to make matters more precise, we started from the notion of the electrical conductivity under isothermal conditions depending on the oxygen pressure in the surrounding atmosphere, for semiconductor oxides.
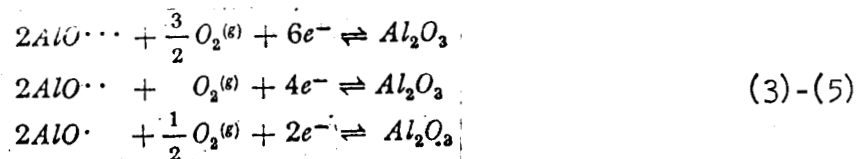
It is known that a series of structural defects appear in ionic crystals which ultimately will lead to the appearance of semiconductor characteristics.

The case we are dealing with refers to ionic crystals having an excess of metal or insufficient oxygen.

The ionic crystal with excess metal (meaning an excess of metal identical with that of the lattice-stoichiometric deffect) can be obtained if the metallic oxide eliminates some quantity of oxygen at elevated temperatures. The void left in the lattice appears in the form of an anionic vacancy O□.., the metal constituting an excess in the lattice or interstices; MO.. (ref. 22).

To satisfy the electric neutrality of crystal, an equivalent number of residual electrons must appear, of which all or only a definite percent appear as conduction electrones of Θ participating in the electrical transport process. These are n type semiconducting electrons. Analogous to the general case mentioned in the literature - pertaining to zinc oxide - our nonstoichiometric alumina is of the semiconducting type n (ref. 23), therefore with an excess of Al or a corresponding deficit of oxygen in the crystal lattice.

Principally, we can consider that the nonstoichiometric alumina is present in order to satisfy the electrical neutrality of the crystal as a result of having lost oxygen or Al^{2+} ions, or AL^+ or metallic Al. We denote by $AlO^{\cdots}$ an interstitial aluminum atom, by $AlO^{\cdots}$ an excess Al^+ ion, and by $AlO^{\cdot}$ an Al^{+2} ion. In an oxygen atmosphere, it stabilizes to a given temperature at termodynamic equilibrium in the form

$$2AlO^{\cdots} + \frac{3}{2}O_2^{(g)} + 6e^- \rightleftharpoons Al_2O_3$$
$$2AlO^{\cdot\cdot} + O_2^{(g)} + 4e^- \rightleftharpoons Al_2O_3 \qquad (3)-(5)$$
$$2AlO^{\cdot} + \frac{1}{2}O_2^{(g)} + 2e^- \rightleftharpoons Al_2O_3$$

which, by the consummation of an equivalent quantity of excess cations is accompanied by the diminution of conductivity.

We denote by $x_{a10}\cdots$ the concentration of residual aluminum atoms, by

$x_{A10}\cdots$ the concentration of monovalent ions, by $x_{A10}\cdots$ the concentration of bi-

valent ions, by x_2 the concentration of electrons, and by P_{O_2} the equilibrium

oxygen pressure in mm Hg. Applying the law of mass action, three cases of

equilibrium are obtained:

$$K_1 = x_{A10}^2 \cdots x_e^6 \, P_{O_2}^{\frac{3}{2}}$$
$$K_2 = x_{2A10}^2 \cdots x_e^4 \, P_{O_2}$$
$$K_3 = x_{A10}^2 \cdot x_e^2 \, P_{O_2}^{\frac{1}{2}}$$

$$(6)\text{-}(8)$$

The constants K_1, K_2, K_3, contain the concentration of Al_2O_3, which, being

in preponderance, can be considered as a constant as far as the analyzed

phenomena is concerned.

Taking consideration of the fact that the electrical conductivity is in

proportion with the electron concentration, it turns out that between the elec-

trical conductivity and the oxygen pressure P_{O_2} different relations exist for the

three cases, in the form

$$-\sigma_1 = K_1' P_{O_2}^{-\frac{1}{5.33}}$$
$$\sigma_2 = K_2' P_{O_2}^{-\frac{1}{6}}$$
$$\sigma_3 = K_3' P_{O_2}^{-\frac{1}{8}}$$

$$(9)\text{-}(11)$$

or, generalizing,

$$\sigma = K P_{O_2}^{-\frac{1}{n}}$$

$$(12)$$

It turns out that between the electrical conductivity and oxygen pressure

there is an inverse variation, characterized in each separate case by the values

of the exponent $1/n$. The correlation becomes more evident after taking the

logarithm, whence

$$\log \sigma = \log K - \frac{1}{n} \log P_{o_2}$$

<div align="right">(13)</div>

By graphical representation of the relation, it is possible to determine 1/n and to decide to which equation the process corresponds.

EXPERIMENTAL PART

The study was carried out on 8.5 t/cm^2 compressed nonstoichiometric aluminum pellets. The apparatus used consisted of an electrical conduction cell formed from razotherm glass equipped with Pt electrodes.

The heating was done by an electric oven supplied by the commercial line through a voltage stabilizer and an autotransfor /mer. The temperature was maintained constant at 380°C and measured with a Pt-PtRh thermocouple. The equilibrium pressure was measured with a Pirani manometer, the electrical resistance of the pellet was with a Tesla megohmeter. By adapting the outlet faucet with a 3-way fitting, the installation was connected to the aggregate vacuum pump, which was furnished with coding traps of dry ice.

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The pressure range in which the conductivity was studied was determined by the indication limits of the Pirani manometer, i.e., 1-10^3 mm Hg. For several determinations of the temperature between 350-400°C, we give in Table 1 and the diagram in figure 2 the values obtained for the temperature at 380°C. The measurements were made at an interval of 1 or 2 hours, in order to stabilize equilibrium.

CONCLUSIONS

From the graphs of $\log \sigma$ vs. $\log P_{O_2}$ we see two distinct slopes. The first corresponds to a ratio $\log \sigma / \log P_{O_2} = 1.5$ found in the interval 10^{-3} - 10^{-2} mm Hg, and the other over 10^{-2} mm Hg corresponding to a ratio of 1: 3.1 having a broken zone between these intervals.
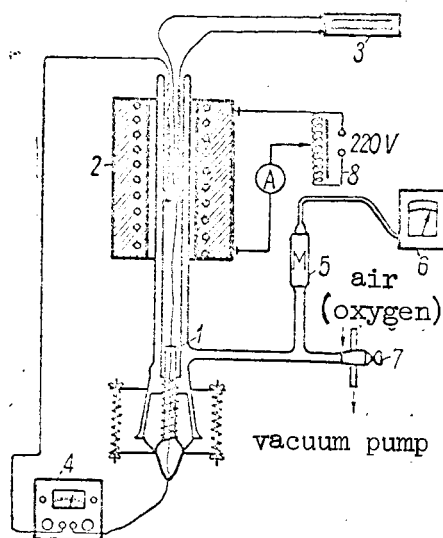
Figure 1. Apparatus for Investigating the Electrical Conductivity as a Function of Oxygen Pressure.
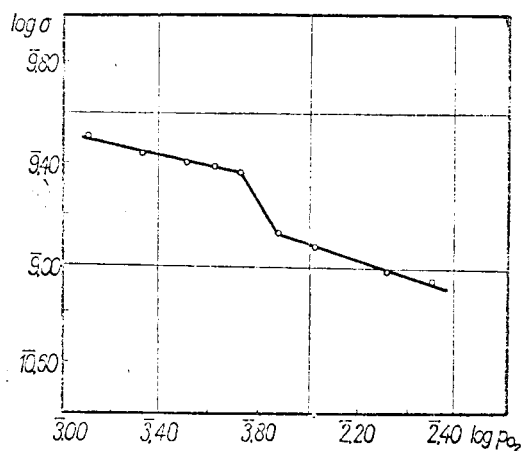
Figure 2. Variation of $\log \sigma$ vs. $\log P_{O_2}$ for Nonstoichiometric Alumina

TABLE 1. VARIATION OF ELECTRICAL CONDUCTIVITY WITH OXYGEN PRESSURE FOR BLACK ALUMINA AT 380°.

No.	P_{O_2} mm Hg	$\log P_{O_2}$	Ω cm $\times 10^8$	$\log \varrho$	$\log \sigma$
1	$1,26 \cdot 10^{-3}$	$\overline{3},100$	8,45	8,513	$\overline{9},487$
2	$2,10 \cdot 10^{-3}$	$\overline{3},322$	3,52	8,547	$\overline{9},453$
3	$3,20 \cdot 10^{-3}$	$\overline{3},498$	3,88	8,589	$\overline{9},411$
4	$4,20 \cdot 10^{-3}$	$\overline{3},623$	4,05	8,607	$\overline{9},393$
5	$5,25 \cdot 10^{-3}$	$\overline{3},720$	4,23	8,626	$\overline{9},374$
6	$7,35 \cdot 10^{-3}$	$\overline{3},866$	7,50	8,875	$\overline{9},125$
7	$1,05 \cdot 10^{-2}$	$\overline{2},021$	8,37	8,923	$\overline{9},077$
8	$2,10 \cdot 10^{-2}$	$\overline{2},322$	10,6	9,025	$\overline{10},975$
9	$3,15 \cdot 10^{-2}$	$\overline{2},498$	11,4	9,057	$\overline{10},943$

Judging from the behavior of the first portion, the variation of log σ vs. log P_{O_2} corresponds with a good approximation (ref. 22) to the process (2), which presumes the presence of metallic Al atoms. As far as the second interval is concerned, the slope of the curve gives the impression of the onset of processes not yet discussed (probably equilibrium was not established or perhaps there is a sudden oxidation in the transition zone, followed by structural reorganization etc.), which could become the subject of further investigation.

Nevertheless, there is no doubt, that inasmuch as neither the ratio 1:5 nor 1:3.1 indicate equilibrium of the Al^+ or Al^{+2} as required by the above curves with a lesser slope (1:6 and 1:8, respectively).

It turns out, therefore, that the presence of nonstoichiometry is due to aluminum atoms dispersed in the alumina mass, imparting n-type semiconducting properties to the sample.

It proves, therefore, that the study of nonstoichiometric has been completed in a favorable manner, consistent with the family of nonstoichiometric oxides and hydrates indicated by Faivre (ref. 4).

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